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Mineral trapping of CO_2 in operated geothermal reservoirs – Numerical simulations on various scales

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Abstract

We present a novel approach for storing CO_2 not only by hydrodynamic trapping within a reservoir but for converting it into the geochemically more stable form of calcite. The combination of CO_2 storage and geothermal energy production is generally feasible because candidate sites are available, anhydrite is transformable into calcite and alkalinity can be provided by fly ashes or even in-situ. However, under the current circumstances the technology is not economical because the storable amount at depth is significantly less than one million tons over the life time of a geothermal heating plant.

Keywords: CO_2 storage; geothermal reservoirs; anhydrite; calcite; mineral trapping

1. Introduction

Various available options for the storage of carbon dioxide (CO_2) in the subsurface have been proposed and discussed for reducing the amount of anthropogenic CO_2 released into the atmosphere. A possible means of reducing these CO_2 emissions is to inject them into structural reservoirs in deep, permeable geologic formations [1], e.g., saline aquifers [2] or depleted gas reservoirs [3]. The concept we present

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here is to store CO_2 not only by hydrodynamic trapping within a reservoir, but to convert dissolved CO_2 into the geochemically more stable form of calcite ($CaCO_3$) in a reaction with calcium obtained from dissolution of anhydrite ($CaSO_4$) and alkalinity from feldspars or fly ash. In this way, the cost for sequestration in deep saline aquifers could be transformed into a benefit when combined with the production of ecologically desirable geothermal heat. Alternatively, geothermal energy can be made more economical, compared to fossil energy sources, by storing CO_2 and trading of emission certificates. The results presented here are based on previous publications [4-5] and carried further with numerical simulations on multiple scales and two location specific studies for Stralsund [6] and Allermöhe [7], respectively. Both are located in Germany and are potential sites for geothermal heat production with storage capacities as well for CO_2.

Numerical simulation is a means for quantifying the entire process of CO_2 storage [8] and deepening the understanding of the detailed chemical processes [9]. We performed numerical simulations on multiple scales reaching from the micro or thin section scale (ca. 1 cm) to the reservoir scale (ca. 10 km). The idea is to provide constraints for smaller-scale models from the larger-scale and derive functionality from smaller-scale models of processes which cannot be resolved in larger scale models, due to restrictions regarding the discretization of the numerical grid.

The geological situation in Germany constrains geothermal energy production at temperatures in excess of about 80 °C to deep saline aquifers. The common arrangement of boreholes is the well doublet, consisting of one well for hot water production and one well for cooled water re-injection. The new concept comprises loading the cooled water with dissolved CO_2. After re-injection into the reservoir, this cold water becomes enriched in calcium, e.g., due to the dissolution of anhydrite. Subsequently, CO_2 precipitates as calcium carbonate. The corresponding chemical reactions are described in the following.

Due to the decreased solubility of anhydrite with temperature, injecting cold water dissolves the mineral in a growing region around the well. The concentrations of calcium and sulphate increase in the water with the dissolution of anhydrite:

$$CaSO_4 \Rightarrow Ca^{2+} + SO_4^{2-} \tag{1}$$

Before re-injection, the produced and cooled brines are enriched with carbon dioxide generating carbonic acid:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \tag{2}$$

The overall reaction, the transfer of anhydrite into calcite, describes the favoured reaction path:

$$CaSO_4 + H_2CO_3 \Leftrightarrow CaCO_3 + 2H^+ + SO_4^{2-} \tag{3}$$

From equation (3) it is obvious that a surplus in acid exists which tends to inhibit calcite precipitation in general. However, if alkalinity is available to buffer the reaction, the solubility product of calcite is exceeded and CO_2 will be trapped as calcite. Alkalinity can be provided either by surface water treatment with fly ash [10-11] or in situ through the weathering of feldspars [4]. The reaction of oligoclase to kaolinite is given here as an example:

$$\begin{aligned} &Na_{0.8}Ca_{0.2}Al_{1.2}Si_{2.8}O_8 + 1.2H^+ + 3.8H_2O \Rightarrow \\ &0.8Na^+ + 0.2Ca^{2+} + 0.6Al_2Si_2O_5(OH)_4 + 1.6H_4SiO_4 \end{aligned} \tag{4}$$

With regard to the feasibility of this new technology the chemical reactions outlined above require answering - by numerical simulations on different scales - the following four key questions:

1. Where are suitable geothermal reservoirs containing anhydrite as a mineral component?
2. Does the transfer of anhydrite into calcite work at all and what are the reaction rates?
3. What are feasible sources of alkalinity and how fast can they be mobilized?
4. What is the overall CO_2 storage potential?

2. Suitable geothermal reservoirs

The stratigraphic horizons, suitable for geothermal heat provision in combination with the storage of CO_2, are identified by the analysis of borehole data. They are selected mainly based on the occurrence of anhydrite and an adequate thickness of potential storage layers. First of all, the amount and distribution of anhydrite within the reservoir needs to be known. Then, the reservoir properties are estimated from the ratio of the clay fraction to the sand fraction. This provides input parameters and geological constraints for the reservoir simulations. However, what needs to be taken into account as well is the fact that the anhydrite content within a reservoir affects the transport properties. Geothermal heating plants require reservoirs with porosities in the order of 20 %. From core samples it is determined that this restricts the amount of anhydrite in the sediments to less than 6 % [5]. In general, suitable potential reservoirs are available in the formations of Buntsandstein, Rhät and Rotliegend with anhydrite as matrix mineral but still being sufficiently permeable.

One candidate site is near Stralsund near the Baltic Sea in North-eastern Germany. Here, a geothermal resource was confirmed in previous studies in Buntsandstein layers at a depth of about 1,520m [6]. This site is used here to demonstrate the potential for CO_2 storage by numerical simulations. There are three wells in the target area which measures 12 km x 6 km. They tap the Detfurth sandstone with a thickness between 33 m and 36 m. Drilling profiles and core samples indicate that the reservoir consists of a weakly consolidated, fine to medium feldspatic quartz sandstone [12]. The cementation consists mainly of calcite and dolomite with a minor amount of anhydrite. Due to the low anhydrite content the hydraulic properties of the reservoir are very good with 24 % porosity and $0.5 \cdot 10^{-12}$ m^2 permeability (~0.5 Darcy).

The second study site is Allermöhe near Hamburg in Northern Germany. Allermöhe was recently considered for the installation of a major geothermal heating station with the Rhaetian sandstone as target aquifer [7]. A well was deepened to 3,300 m and the reservoir was reached providing 70 m of sandstone with a temperature of 125 °C. However, initial plans for a geothermal heating plant at Allermöhe were abandoned: because unexpectedly, the Rhaetian sandstone proved to be extensively mineralized by anhydrite, reducing porosity and permeability to values too low for an economical use. Here, this location serves as an additional test site for the suggested technology with regard to the inherent anhydrite amount in the reservoir.

3. Transformation of anhydrite into calcite

The transformation of anhydrite into calcite is critical for the feasibility of this new technology. Three aspects of the reaction are particularly important: (1) the acidity produced in the system which limits the reaction, (2) the transformation rate, i.e., the dissolution kinetics of anhydrite and the precipitation kinetics of calcite and (3) alterations of the pore space due to dissolution of anhydrite and precipitation of calcite.

3.1. Batch reaction experiments and calculations

In batch experiments in the laboratory, the dissolution kinetics of natural anhydrite is studied far from the conditions of thermodynamic equilibrium (saturation index SI < -0.4). Further, to prove the feasibility of the transformation of anhydrite into calcite additional batch experiments were performed [5]. After termination of each experiment the suspension was freeze dried and the mineral phases quantified with X-ray diffraction (XRD).

Based on these laboratory experiments, we performed calculations of the batch reaction with PHREEQC [13] for deducing the limiting pH of the brine and also confirming theoretically the feasibility of the transformation of anhydrite into calcite. It is shown that the reaction of interest takes place at a pH as low as 5.5 [5]. Hence, the transformation is not limited to extremely high pH values but occurs also under boundary conditions that exist in the saline aquifers targeted.

In the kinetic simulations using the program PHREEQC, a rate law for the dissolution of anhydrite and the precipitation of calcite was applied according to Plummer et al. [14]. Both our experiment and calculations prove that calcite is formed under different boundary conditions [5].

3.2. Core flooding experiment

Dissolution of anhydrite and growth of calcite can be translated into the associated variations of porosity. Following the assumption of equation (3) that 1 mole of anhydrite, with a molar volume of $4.59 \cdot 10^{-5}$ m^3 mol^{-1}, is transferred into 1 mole of calcite, with a molar volume of $3.69 \cdot 10^{-5}$ m^3 mol^{-1}, a net increase in porosity is determined of about 20 %. Even though porosity and permeability are closely related properties, a porosity increase does not result necessarily in a corresponding permeability increase. If, for instance, precipitation of calcite occurred primarily in the pore throats the net permeability of the reservoir sandstone might also decrease. Therefore, a core flooding experiment was performed with original reservoir rock [5] for studying the relation between variations of porosity and permeability in the system.

Permeability changes of the sample were continuously recorded by a capacitive differential pressure gauge. As an important result it is observed that the average permeability of the core increases continuously with flooding time after a short initial period of a slight permeability decrease [5]. As expected, the combined reaction of anhydrite dissolution and calcite precipitation resulted in an increase of both porosity and permeability.

4. Suitable sources of alkalinity

From equation (3) it becomes obvious that availability of alkalinity might be a requirement to mineralise CO_2 to calcite in geothermal reservoirs. Alkalinity buffers the reaction, and the solubility product of calcite can be exceeded. The overall reaction is pushed towards the products. Alkalinity may be provided either in situ through the weathering of feldspars or at the surface by water treatment with fly ashes.

4.1. In-situ alkalinity source

Numerical batch simulations are performed for the potential site at Stralsund with its confirmed geothermal resource [6]. At first, the thermodynamic equilibrium of the chemical reactions was studied with regard to the technical process planned for this technology. The formation water is cooled, enriched with varying amounts of CO_2 and again brought into contact with the reservoir minerals. Therefore the

simulations were performed at a temperature of 25 °C consistent with the assumption that the relevant reactions occur within that part of the geothermal reservoir where the cool injection temperature prevails.

As expected, the pH decreases with an increasing amount of added CO_2 [5]. Therefore, weathering of plagioclase providing additional alkalinity is required for calcite precipitation so that CO_2 may be precipitated as calcite. However, plagioclase dissolution only is insufficient. For increasing the rate of dissolution and in turn increasing the buffering capacity, kaolinite needs to be formed as a secondary silicate phase. It is found that anhydrite is not a chemical driver of the reaction, which can be deduced from the fact that its dissolution is constant and independent of the added CO_2 [5]. The amount of dissolved anhydrite solely depends on the difference between the formation temperature and the temperature of the injected water.

4.2. Alkalinity provided from fly ash

As outlined above, surface treatment of the geothermal brine with fly ash provides an alternative supply of alkalinity for the transformation of anhydrite into calcite. Our laboratory experiments show [10-11] that alkalinity is available from fly ash and that reaction rates are high. Recent batch reaction simulations of the experiments emphasize that calcite is precipitated from a mixture of fly ash treated geothermal formation water with formation water enriched by the technologically maximum amount of CO_2. In this case calcite is produced even without alkalinity supplied from rock forming minerals. As before, anhydrite dissolution is important for keeping the reservoir pore space open. The results outline the geochemical framework for the technical use not only of lignite ashes for CO_2 sequestration but also of alkaline combustion residues in general.

5. Numerical simulations and determined CO_2 storage potential

Numerical simulation allows quantifying the entire process of CO_2 storage and provides a deeper understanding of the involved chemical processes. We performed numerical simulations on multiple scales, the relevant scales reaching from the micro or thin section scale (≈ 1 cm) to the reservoir scale (≈ 10 km).

As a starting point for further reactive transport simulations, we performed batch reaction simulations (no spatial scale). Simulations on the smallest, the micro scale, are used to study the overall process of mineral dissolution and precipitation further. Core flooding experiments were used to calibrate the numerical tools [5]. The borehole scale was studied with care because the immediate vicinity of the wells in a geothermal installation is particularly vulnerable to permeability decreases resulting from mineral reactions and the wells comprise the major investment of a geothermal heating plant. Numerical reservoir-scale simulations are required for predicting and quantifying the amounts of storable CO_2.

The batch simulations were performed consistent with the technical process planned for this technology as described in section 4.1. The formation water is cooled, enriched with CO_2 and brought into contact with the reservoir minerals again.

The numerical experiments on the micro-scale are generic experiments (Fig. 1). The idea is that an ion, a water molecule or a package of mineralised solution can only react with one mineral at a time because it can only be at one location at a time. In reactive transport simulation, a specific but averaged and homogenised mineral assemblage is commonly considered for each model element or cell. However, understanding the chemistry of the mineralization process may require appreciating the fate of a volume compartment of water as it gets in contact and reacts with distinct minerals in a certain sequence in time. The applied model is on the scale of 1 cm × 3 cm and discretised into 1 mm × 1 mm cells. One of a

number of minerals was assigned to each model element (quartz, plagioclase, K-feldspar or anhydrite; Fig. 1).

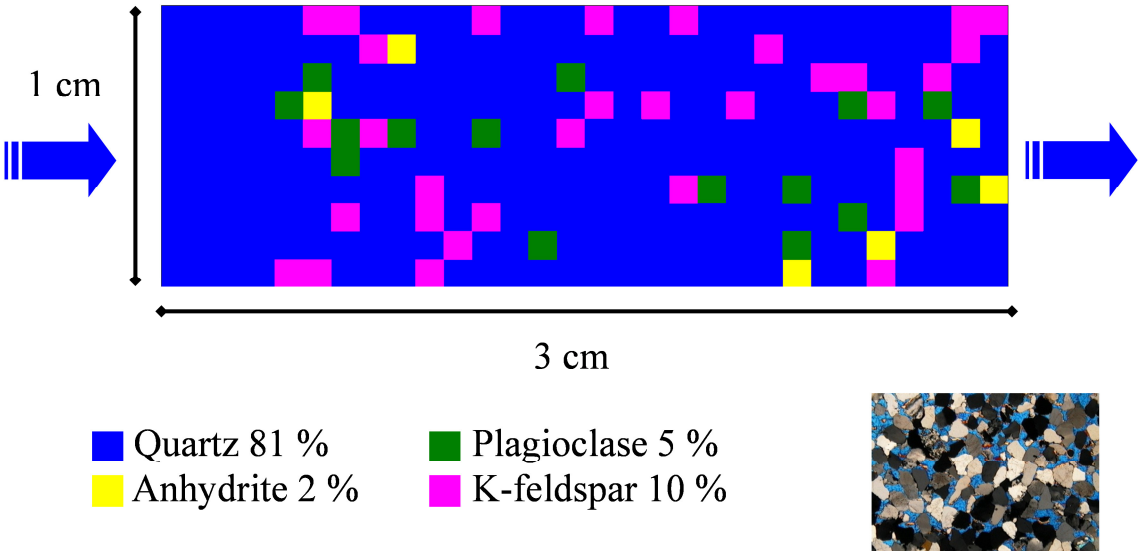

Fig. 1. Model for numerical simulations on the micro scale. The total extent is 1 cm × 3 cm with cells of 1 mm^2. The mineralogical assemblage reflects the conditions at the Stralsund location [6], [12]

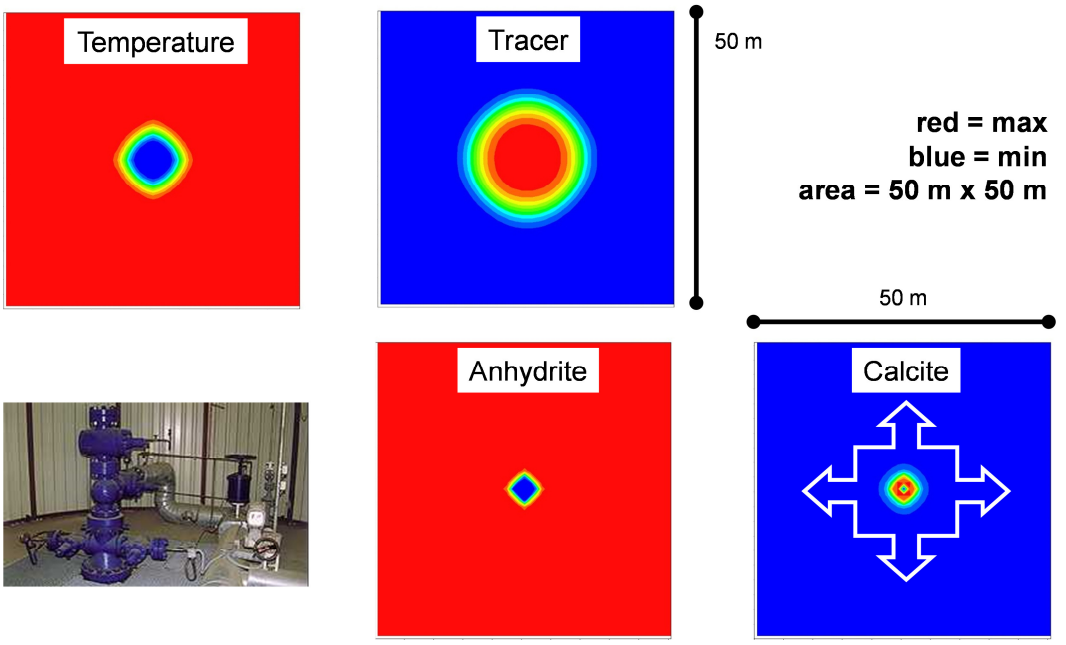

Fig. 2. Model for numerical simulation on the borehole scale showing an advancing reaction front of dissolving and precipitating calcite in the cooled and warm regions, respectively

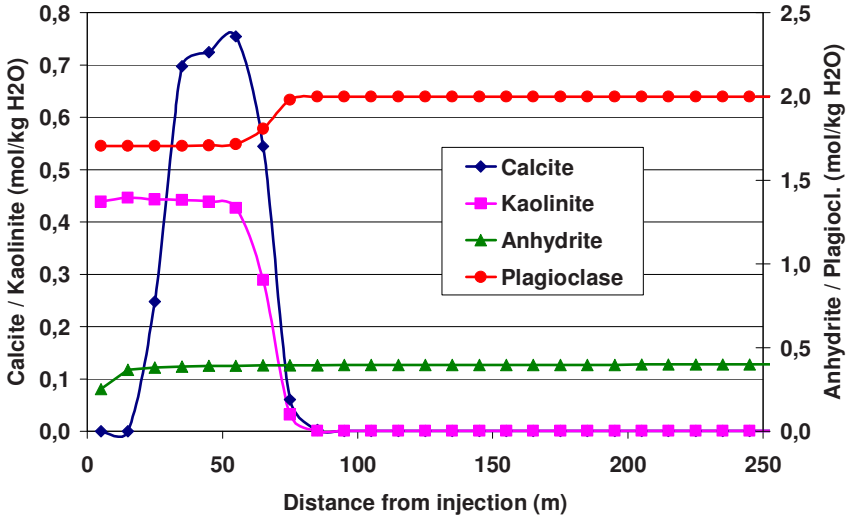

Fig. 3. Model for numerical simulation on the reservoir scale showing a moving reaction front of precipitated calcite

Two scenarios are modelled on this micro-scale: The first one as described before with one mineral for each model cell. In the second one, all available mineral phases occur in each model cell as is the common approach in reactive transport modelling. After passage through the rock the waters of these two scenarios exhibit identical chemical compositions. However, the resulting rock alteration assemblage is significantly different for the two models. As mentioned above, the dissolution of plagioclase is essential for the formation of calcite. It is striking that the common case of reactive transport simulation produces a planar calcite reaction front moving through the system. In the generic model the resulting calcite distribution is heterogeneous and permanent. Therefore we assume that heterogeneity on the micro-scale has important effects for the larger-scale.

Tests on the borehole scale with regard to the transformation of anhydrite into calcite are shown in Fig. 2. Like the laboratory experiment, the numerical model proves that anhydrite can be transferred successfully into calcite. The spatial distribution of temperature, a tracer, anhydrite and calcite is shown, which is caused by the simulated water re-injection. The model area is 50 m × 50m with the borehole in the centre. It can be seen how the cooler temperature of the injected water has spread around the injection well. At the same time the non-reactive tracer (incorporated to detect the conservative transport process) has advanced even further away from the well.

Due to the thermal capacity of the solid rock, the thermal front advances slower than the transported dissolved ions. Over time, the injection of cold water reduces the anhydrite content in the reservoir rock to zero within a cylinder around the well. The pH of the injected water is fixed and in-situ buffering is disregarded in this case. The lower right of Fig. 2 shows the successful storage of CO_2 in form of calcite. This occurs as a result of the increase of the concentrations of calcium and carbonate ions in the injected brine. However, what can also be observed is a moving calcite front (as was observed in the models on the micro scale). As soon as the anhydrite is dissolved completely the decreased calcium concentration in this region results in a re-dissolution of calcite.

As mentioned above, three boreholes are available for the candidate site Stralsund allowing for two different arrangements: (1) two wells used for production and the third one for injection or (2) two boreholes used for injection and the third one for production. This corresponds to thermally and

hydraulically affected reservoir rock volumes of approximately 220 million m^3 and 370 million m^3, respectively. The thermally affected region delineates the volume where anhydrite dissolution occurs and calcite precipitates. For the Stralsund site, Fig. 3 shows results of numerical simulations including chemical reactions on the reservoir scale. As seen before, anhydrite and plagioclase dissolve; kaolinite and calcite precipitate. We observed a moving calcite reaction front, similar as in the micro- and borehole-scale simulations.

Based on all results of the presented numerical simulations, we calculated mass balances for the sites at Stralsund and Allermöhe. In these calculations, we assume that geothermal energy production lasts for 65 years (as suggested by reservoir simulations for Stralsund) with 57 million m^3 water pumped over the entire life time at a rate of 100 m^3 h^{-1}. The same scenario is assumed for Allermöhe, even though such an amount of produced and injected water is unlikely due to the cementation in the aquifer.

If we consider a maximum pressure within the surface installation of a geothermal plant of 1 MPa, the solubility of CO_2 in the formation waters are 210,000 t for Stralsund and 325,000 t for Allermöhe. On the same time frame, the dissolution of anhydrite in the formation water amounts to 7,800 t and 33,000 t CO_2 equivalents for Stralsund and Allermöhe, respectively. The CO_2 equivalent calculation is based on equation (3) and the fact that 1 mole of dissolved anhydrite results in 1 mole of precipitated calcite. If there was a means for removing Ca and SO_4 completely from the solution aboveground, the solubility of anhydrite could be increased further and the precipitated equivalents of CO_2 would increase up to 123,000 t for Stralsund and 130,000 t for Allermöhe.

Under the assumption that it might be possible to reach thermodynamic equilibrium on the technological time frame regarding the available in-situ alkalinity the reaction rates of calcite, anhydrite, plagioclase and kaolinite sum up to 126,000 t of CO_2 equivalents for the Stralsund site. This calculation cannot be performed for Allermöhe due to lacking information about water composition and reservoir mineralogy. For alkalinity provided through surface treatment from fly ash the thermodynamic equilibrium would result in 22,000 t CO_2 equivalents.

What can be deduced from the described numerical simulations and mass balance calculations is that the storage capacity depends on the most restrictive constraints, i.e., the contents of anhydrite and feldspar in the rock and CO_2 in the re-injected water. Calculations are performed with respect to the contents of anhydrite (assuming that anhydrite is transformed completely into calcite), feldspar (assuming that feldspar dissolves completely and provides the alkalinity required for the transformation) and the solubility of CO_2 in brine. Finally, for a scenario of 65 years of geothermal energy production, the largest amount of stored CO_2 equivalents is calculated to 130,000 t. Compared to the storage potentials in such reservoirs provided by hydrodynamic trapping only, this is by far too little and therefore uneconomical.

In order to achieve a zero emission power plant (i.e. equal amounts of CO_2 trapped and emitted during the lifetime of the geothermal plant including construction and demolition) approximately 150,000 t of CO_2 [15] need to be trapped as calcite. From the discussion above it can be deduced that this goal would be just achievable within the best case assumption.

6. Conclusions

We studied an alternative technology for combining geothermal energy production with mineral trapping of carbon dioxide in geological reservoirs. With regard to the four key questions posed in the introduction we conclude that this technology is generally feasible because: (1) candidate sites with anhydrite bearing reservoirs are available; (2) anhydrite can be transformed into calcite, associated even with a permeability increase and (3) alkalinity may be provided either in-situ from aluminium silicates or on the surface by treatment of the produced brines with fly ash. But (4) the storage capacities of CO_2 amount to significantly less than 1 million tonnes over the lifetime of a geothermal plant compared to

above 10 million tonnes if the same reservoir were used for hydrodynamic trapping of CO_2 only. Under the current circumstances the mineral trapping technology of CO_2 in operated geothermal reservoirs is uneconomical due to this small storage potential.

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